APPENDIX A

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Baton Rouge, LA Unit 1
Single Absorption Sulfuric Acid Regeneration Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases.

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$
$E = (K / Xe) - K$
Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

  Equation 2 (rolling 3 hour average SO_2 emissions)
  $Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$
  $E_{3hravg} = (K / Xe_{3hravg}) - K$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)

    $$Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$$

    $$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$$

  - The number of operating minutes for the day will be summed (T_{day},)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 1.9 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	460 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	920 or IPS-4 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 6, and LDEQ of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Baton Rouge, LA, Unit 2
Hybrid Single Absorption Sulfuric Acid Regeneration Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$$
$$E = (K / Xe) - K$$

Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

Equation 2 (rolling 3 hour average SO_2 emissions)

$$Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$$
$$E_{3hravg} = (K / Xe_{3hravg}) - K$$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)

    $$Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$$

    $$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$$

  - The number of operating minutes for the day will be summed (T_{day},)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 2.2 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	460 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	920 or IPS-4 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Process conditions and / or configuration may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
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General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

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- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Baytown, Texas
Single Absorption Sulfuric Acid Regeneration Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

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The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

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"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases.

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$$
$$E = (K / Xe) - K$$

Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

  Equation 2 (rolling 3 hour average SO_2 emissions)

  $$Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$$
  $$E_{3hravg} = (K / Xe_{3hravg}) - K$$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)

    $$Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$$

    $$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$$

  - The number of operating minutes for the day will be summed (T_{day},)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 2.2 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	920 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	920 or IPS-4 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 6, and TCEQ of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Dominguez Plant, Long Beach, California
Sulfuric Acid Regeneration Plant with Double Absorption

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean the annual SO2 allocation determined by the South Coast Air Quality Management District's Regional Clean Air Incentives Market (RECLAIM), as defined in Regulation XX of the South Coast Air Quality Management District Rules.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$$
$$E = (K / Xe) - K$$

Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

Equation 2 (rolling 3 hour average SO_2 emissions)

$$Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$$
$$E_{3hravg} = (K / Xe_{3hravg}) - K$$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.5 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

Compliance with the Long Term Limit, which is an annual allocation of SO2, shall be done with the existing CEMS that currently complies with South Coast Air Quality Management Districts RECLAIM regulations, as defined in Regulation XX of the South Coast Air Quality Management District Rules.

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Thermo Environmental (or equivalent)	42i (or equivalent)	Dual range: Normal: 0 – 200 ppm SO_2 SSM: 0 – 1,000 ppm SO_2
Converter Inlet	Thermo Environmental (or equivalent)	42iHL (or equivalent)	Single range: 0 – 12 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). The proposed sampling location is in a section of vertical straight duct on the suction side of the main gas blower. A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In accordance with existing South Coast Air Quality Management District RECLAIM regulations, for every hour of invalid data, missing data must be substituted following the procedures in Rule 2011, Appendix A, Chapter 2, Section E – Missing Data Procedures. The existing stack CEMS complies with these procedures. The blower inlet analyzer system shall also follow these procedures for every hour of invalid data

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 9, and SCAQMD of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Hammond, Indiana
Sulfuric Acid Regeneration Plant with Double Absorption

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases.

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$$
$$E = (K / Xe) - K$$

Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

Equation 2 (rolling 3 hour average SO_2 emissions)

$$Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$$
$$E_{3hravg} = (K / Xe_{3hravg}) - K$$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.5 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)

    $$Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$$

    $$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$$

  - The number of operating minutes for the day will be summed ($T_{day,}$)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 2.5 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	460 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	460 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 5, IDEM and HDEM of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Houston, TX Unit 2
Single Absorption Sulfuric Acid Regeneration Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases.

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$
$E = (K / Xe) - K$
Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

Equation 2 (rolling 3 hour average SO_2 emissions)
$Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$
$E_{3hravg} = (K / Xe_{3hravg}) - K$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)
    $Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$
    $E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$

  - The number of operating minutes for the day will be summed ($T_{day,}$)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 1.8 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	920 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	920 or IPS-4 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 6, and TCEQ of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Houston, TX Unit 8
Single Absorption Sulfuric Acid Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

Sulfur dioxide emissions from the Houston 8 sulfuric acid unit will be monitored in accordance with the requirements of the existing NSPS for sulfuric acid plants except as noted in this AMP. The CEMS will demonstrate compliance on a real-time basis with the SO_2 emissions standard (as lbs of SO2 per ton of 100% sulfuric acid produced) using stack SO_2 and O_2 analyzers. The purpose of this AMP is to document the calculation methods that will be utilized to demonstrate compliance with regulations as modified by the Consent Decree.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases.

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

Pt. 60.84 Emissions Monitoring.

Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 and O_2 analyzers at the exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$Xe = (0.209 - MO2 - MSO2) / (0.209 - MO2 + 0.186 \times MSO2)$
$E = (K / Xe) - K$
Where:

Xe = fractional conversion efficiency
MO2 = fractional concentration of O_2 at the stack, dry basis
MSO2 = fractional concentration of SO_2 at the stack, dry basis
E = SO_2 emission rate in lb / ton of 100 % acid produced
K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the O_2 and SO_2 concentrations at the exit stack.
- Once every five minutes, the system will sample the latest O_2 and SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $MO2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of O_2 at the stack ($MO2_{3hravg}$).
- $MSO2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($MSO2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

  Equation 2 (rolling 3 hour average SO_2 emissions)
  $Xe_{3hravg} = (0.209 - MO2_{3hravg} - MSO2_{3hravg}) / (0.209 - MO2_{3hravg} + 0.186 \times MSO2_{3hravg})$
  $E_{3hravg} = (K / Xe_{3hravg}) - K$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the O_2 or SO_2 monitors, the O_2 or SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the O_2 and SO_2 concentrations at the exit stack will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the O_2 and SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $MO2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of O_2 at the stack.
  - $MSO2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

Equation 3 (daily average SO_2 emissions)

$Xe_{daily\ avg} = (0.209 - MO2_{daily\ avg} - MSO2_{daily\ avg}) / (0.209 - MO2_{daily\ avg} + 0.186 \times MSO2_{daily\ avg})$

$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$

- The number of operating minutes for the day will be summed ($T_{day,}$)
- E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 1.7 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the O_2 or SO_2 monitors, the O_2 or SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack SO_2	Ametek Photometric Analyzer (or equivalent)	920 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 3,600 ppm SO_2
Stack O_2	Ametek Oxygen Analyzer (or equivalent)	920 (or equivalent)	Single range: 0 – 20.9 % O_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- SO_2 in the exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- O_2 in the exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Orsat test or other method (e.g. portable analyzer)
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exception. Given that one or both of the stack CEMS is out of service, the most recent hourly reading(s) will be substituted for the 12 (24) five-minute readings that would otherwise be taken if the system was operating normally

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring Plan for SO_2 Emissions
Rhodia Inc. Martinez, California
Single Absorption Sulfuric Acid Regeneration Plant with Scrubber

Justification for Using an Alternative Monitoring Plan (AMP) for SO_2 emissions

The regulations that established the NSPS for sulfuric acid plants are over 30 years old. At the time, the regulatory standard was established as 4 lb of SO_2 emissions per ton of 100 % sulfuric acid produced, and compliance with the standard was to be demonstrated using a calculation similar to Equation 1 below. Regulations required the use of a CEMS to measure SO_2 concentration at the stack (M2), but only required measurement of SO_2 entering the converter by suitable method three times per calendar day. Plants typically rely on the use of a Reich test once per shift to establish the SO_2 concentration entering the converter (M1). While the stack measurement represented a nearly continuous real time indication of the stack concentration, performing a Reich test once per shift for the converter inlet concentration provides little more than a random sample once every eight hours.

The methodology proposed in this AMP will provide a more continuous real-time indication of compliance by using a process analyzer to measure the converter inlet SO_2 concentration. While this analyzer will be nearly identical to the CEMS that is commonly used at the stack, it will not be able to meet all of the standards that are usually applied to a CEMS because of the process conditions and / or physical limitations of an existing facility. For example, it is not feasible to modify the existing ductwork around the analyzer to meet the normal guidelines for straight runs of pipe upstream / downstream of the analyzer. We believe that the disadvantages (places where the analyzer is not quite up to CEMS standards) are far outweighed by the advantages of using a real time instrument, rather than a periodic Reich test, to measure the converter inlet concentration. Rhodia will use best professional judgment to ensure the analyzer located at the converter inlet provides representative data.

Except as noted in this document, the objective of this proposed AMP is to maintain the process analyzer at the converter inlet in a manner that is similar to the stack CEMS, as set forth in 40 CFR Part 60, Appendix B and F.

Definitions

"CEMS" or "Continuous Emission Monitoring System" shall mean equipment that continuously measures and records the concentration and/or emission rate of a pollutant, in the units specified by the emission limit concerned.

"Long-Term Limit" shall mean a sulfur dioxide (SO_2) emission limit for a sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over all Operating Hours in a rolling 365-day period.

"Malfunction" shall mean, consistent with 40 C.F.R. § 60.2, any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment, process equipment, or a process to operate in a normal or usual manner, but shall not include failures that are caused in part by poor maintenance or careless operation.

"Operating Hours" shall mean periods during which sulfur or sulfur-bearing compounds, excluding conventional fossil fuels such as natural gas or fuel oil, are being fed to the furnace.

"Short-Term Limit" shall mean the SO_2 emission limit for each sulfuric acid plant expressed as pounds per ton of 100% sulfuric acid produced ("lbs/ton"), averaged over each rolling 3-hour period. Except for periods of Startup, Shutdown and Malfunction, the Short-Term Limits established under this Consent Decree shall apply at all times.

"Shutdown" shall mean the cessation of operation of a sulfuric acid plant for any reason. Shutdown begins at the time sulfur or sulfur-bearing feeds, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace ceases

"Startup" shall mean the 24-hour period at any sulfuric acid plant beginning when the feed of sulfur or sulfur-bearing materials, excluding conventional fossil fuels such as natural gas or fuel oil, to the furnace commences after a main gas blower shutdown.

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Compliance with the Long-Term Limit and Short-Term Limit defined by the Consent Decree will be demonstrated using SO_2 analyzers at the converter inlet and exit stack using the following equation. Refer to additional discussion below the equation for specific details related to data input and calculation.

Equation 1

$Xe = (M1 - M2)/(M1 - 1.5 \times M1 \times M2)$
$E = (K / Xe) - K$
Where:

- Xe = fractional conversion efficiency
- M1 = fractional concentration of SO_2 entering the converter
- M2 = fractional concentration of SO_2 at the stack
- E = SO_2 emission rate in lb / ton of 100 % acid produced
- K = 1306 = (2000 lb / ton) x (64 lb / lbmol SO2)/(98 lb / lbmol H_2SO_4)

Short-Term Limit

The following procedure and calculation will be performed once every five minutes during all Operating Hours, except periods of Startup, Shutdown or Malfunction, to demonstrate compliance with the Short-Term Limit for SO_2.

- At any given time the system will maintain an array consisting of the 36 most recent samples of the SO_2 concentrations at the converter inlet and at the exit stack.
- Once every five minutes, the system will sample the latest SO_2 concentrations, add the recent readings to the array and delete the oldest readings. If the unit is not operating then the array of data will not change.
- $M1_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 entering the converter ($M1_{3hravg}$).
- $M2_{3hravg}$ will then be calculated as the arithmetic average of the 36 most recent data samples for the fractional concentration of SO_2 at the stack ($M2_{3hravg}$).
- The rolling 3 hour average SO_2 emissions (E_{3hravg}) will then be calculated per Equation 2.

  Equation 2 (rolling 3 hour average SO_2 emissions)
  $Xe_{3hravg} = (M1_{3hravg} - M2_{3hravg})/(M1_{3hravg} - 1.5 \times M1_{3hravg} \times M2_{3hravg})$
  $E_{3hravg} = (K / Xe_{3hravg}) - K$

- The production unit will be deemed to be operating in compliance with the Short Term Limit if $E_{3hr\text{-}avg}$ does not exceed 3.0 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours except periods of Startup, Shutdown or Malfunction.

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunctions, breakdowns, and repairs.

Long-Term Limit

The following method will be used to calculate the daily average lb of SO_2 per ton of 100% sulfuric acid, and the number of Operating Hours for the calendar day.

- Once every five minutes during all Operating Hours, the SO_2 concentrations (converter inlet and exit stack) will be sampled and this time will be counted as five operating minutes. If the unit is not operating, then the SO_2 concentrations will not be sampled.

- The daily average will be calculated as follows for each calendar day:
  - $M1_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 entering the converter.
  - $M2_{daily\ avg}$ will be calculated as the arithmetic average of the sample population for the fractional concentration of SO_2 at the stack
  - $E_{(daily\ avg)}$ will then be calculated using Equation 3.

    Equation 3 (daily average SO_2 emissions)

    $$Xe_{daily\ avg} = (M1_{daily\ avg} - M2_{daily\ avg})/(M1_{daily\ avg} - 1.5 \times M1_{daily\ avg} \times M2_{daily\ avg})$$

    $$E_{daily\ avg} = (K / Xe_{daily\ avg}) - K$$

  - The number of operating minutes for the day will be summed ($T_{day,}$)
  - E_{dayavg} and T_{day} will be used to calculate a 365-day rolling average of lb/ton. The daily averages will be weighted by the number of operating minutes per day, as per Equation 4.

Once the system has been in operation for 365 days, compliance with the Long Term Limit (365-day rolling average) SO_2 emission rate will be calculated using Equation 4.

Equation 4

$$E_{365avg} = \frac{\sum [E_{dayavg} * T_{day}]}{\sum T_{day}}$$

The production unit will be deemed to be operating in compliance with the Long-Term Limit if E_{365avg} does not exceed 2.2 lb of SO_2 per ton of 100% sulfuric acid produced during all Operating Hours

During routine calibration checks and adjustments of the SO_2 monitors, the SO_2 measurement will be "frozen" at its pre-calibration level. Refer to System Maintenance and Malfunction for guidance during CEMS malfunction, breakdowns, and repairs:

Pt. 60.84 Emissions Monitoring Pt. 60, App. B, Spec. 2, Section 6.0 (Stack and Converter Inlet Analyzers)

Rhodia proposes to use the following stack analyzer specifications to satisfy the requirements of Pt. 60.84 and Pt. 60, App. B, Spec. 2, Section 6.0. The stack analyzer span must be capable of accommodating elevated emissions during startup. Specifications for the analyzer located at the converter inlet are based on Rhodia's experience with process analyzers at these locations.

An equivalent analyzer may be substituted for any reason.

Location	Manufacturer	Model Number	Range
Stack	Ametek Photometric Analyzer (or equivalent)	460 (or equivalent)	Dual range: Normal: 0 – 500 ppm SO_2 SSM: 0 – 4,000 ppm SO_2
Converter Inlet	Ametek Photometric Analyzer (or equivalent)	920 or IPS-4 (or equivalent)	Single range: 0 – 15 % SO_2

Pt. 60, App. B, Spec. 2, Section 1.0 (Stack and Converter Inlet Analyzers)

Initial compliance certification required only if the analyzer is replaced or if system modifications require one to be performed. Additional detail and exceptions noted below under System Modifications below.

Pt. 60, App. B, Spec. 2, Section 8.0 (Converter Inlet Analyzer)

Rhodia will select the optimum location to obtain representative SO_2 readings from this location. Turbulence near the blower exit and elevated temperature at the converter inlet may require an analyzer measurement location that differs from the requirements of this section (e.g. pollutant stratification). A pollutant stratification test is not warranted for this application because (a) process conditions make it extremely unlikely that stratification could occur, and (b) the samples obtained under this monitoring plan are the same as would be obtained under the NSPS, except that the instrument will typically take 288 samples per day rather than the 3 required by the NSPS. Therefore, no new stratification risk is introduced by this method, but the instrument will typically take about 100 times as many samples.

Pt. 60, App. B, Spec. 2, Section 16.0 (Converter Inlet Analyzer)

Rhodia will use the Alternative Relative Accuracy Procedure provided in Section 16.2.1 (i.e. conduct a cylinder gas audit).

Pt. 60, App. F, Spec. 2, Section 5.0 (Converter Inlet Analyzer)

Rhodia will use quarterly cylinder gas audits (i.e. four per year) to satisfy the requirements of this section.

System Maintenance and Malfunction

Except for monitoring malfunctions, associated repairs, and required quality assurance or control activities (including calibration checks and required zero and span adjustments), the plant shall conduct monitoring in continuous operation during all Operating Hours as defined above

In the event of a CEMS malfunction of greater than 24 hours:

- Exit stack gas will be sampled and analyzed at least once per hour, during all Operating Hours.. Sampling will be conducted by Reich test or other method (e.g. portable analyzer).
- Converter inlet gas will either be sampled, or estimated using engineering judgment, at least once every four hours during all Operating Hours.
- Compliance with the Short-Term Limit and Long-Term Limit shall be verified by using these data and Equations 2, 3, and 4 with the following exceptions. If the stack CEMS is out of service, the most recent hourly reading will be substituted for the 12 five-minute readings that would otherwise be taken if the system was operating normally. Similarly, if the converter inlet SO_2 analyzer is out of service, the most recent four-hour reading will be substituted for the 48 five-minute readings that would otherwise be taken if the system was operating normally.

In the event of an analyzer malfunction, a like-kind replacement may be used while repairs are being made. A cylinder gas audit (CGA) must be performed on the replacement analyzer as soon as is practicable after it is placed in service. The daily calibration drift requirement would also apply to the replacement analyzer.

System Modifications

Significant replacement, modification, or change in certified CEMS equipment may require a complete recertification. If a recertification is required, it will be conducted within 90 days. Examples include:

- Change in location or orientation of the sampling probe or site
- Complete replacement of an existing continuous emission monitoring system.

When replacing components that can alter the physical characteristics or conditioning of the sample in the field, a CGA is required. The following activities will require a CGA to be performed before returning the analyzer to service.

- Replacement of the analyzer
- Detector replacement
- Replacement of equipment associated with the detector

The following activities are not expected to trigger a CGA. However, it is recommended that a Calibration Drift check be performed before returning to service.

- Filter replacement
- Data Recorder Repairs
- Tubing replacement

General guidance: When replacing components or devices that do not affect the physical characteristics or handling of the gas in the field such as data recorders, a CGA is not required. A calibration drift check normally should be conducted. If the repaired component affects the transport of the gas to the analyzer, such as replacing tubing, a leak check should be conducted.

Alternative Monitoring System

The monitoring system proposed in this Alternative Monitoring Plan is expected to be a significant improvement over the monitoring requirements contained in the NSPS for sulfuric acid plants. However, the real-time calculation of SO_2 emissions is dependent upon the use of an SO_2 analyzer in the inlet duct to the converter, and the maintenance of that analyzer to approximately the same performance standards normally applied to the stack SO_2 CEMS. This is an unproven application of this technology, and there is some risk that the converter inlet SO_2 analyzer will not be able to perform as required despite the best efforts of Rhodia and the instrument manufacturer.

If Rhodia and the instrument manufacturer are unable to make the system operate to the indicated standards because the converter inlet SO_2 analyzer is unreliable and / or inaccurate in this application, then Rhodia will promptly notify EPA Region 9, and BAAQMD of its determination and proceed as follows:

- Rhodia will immediately begin meeting its SO_2 emissions monitoring requirements in accordance with 40 CFR Part 60, Subpart H, except that the SO_2 concentration at the converter inlet will be analyzed six times per day rather than the three times per day specified in the regulations.
- Rhodia will provide whatever information is requested by EPA regarding the determination that the converter inlet SO_2 analyzer can not meet the necessary performance standards.
- Rhodia will work with EPA to determine whether real time measurement of SO_2 emissions (in lbs / ton of acid) can be readily accomplished through other means without the use of an SO_2 analyzer at the converter inlet.